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ARTICLE

Chemical synthesis of high quality epitaxial vanadium dioxide films with sharp electrical and optical switch properties

A. M. Makarevich,^{a,b,†} I. I. Sadykov,^a D. I. Sharovarov,^c V. A. Amelichev,^b A. A. Adamenkov,^b D. M. Tsybarenko,^a A. V. Plokhiih,^c M. N. Esaulkov,^d P. M. Solyankin^e and A. R. Kaul^{a,b}

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The effective preparation method of epitaxial VO₂ films on the r-Al₂O₃ substrates based on the MOCVD technique and post-deposition annealing is described. The composition, orientation and morphology of the films obtained were investigated by Raman spectroscopy, XRD, EBSD, XPS, SEM and AFM methods. The samples obtained demonstrate high crystal quality and excellent physical properties: sharp metal-insulator (>10⁴ resistance change) and intensive optical reflectivity (IR and THz regions) transitions. The model of VO₂ films recrystallization based on the peritectic decomposition of intergrain vanadium oxide phases is proposed.

Introduction

Among oxide materials demonstrating metal-insulator transition (MIT) the vanadium dioxide is of special interest because it shows reversible ultrafast (10⁻¹² - 10⁻¹⁵ s) temperature driven MIT close to the room temperature (68°C in the bulk). At this temperature the vanadium dioxide transforms from a low temperature insulating monoclinic phase to a high temperature metallic rutile phase. This transformation is coupled with five order of magnitude resistance change (for single crystals).¹ The critical temperature (T_c) of vanadium dioxide is the function of V-V distance in crystal structure and it can be changed by high pressure and doping.² The phase transition in VO₂ thin films can be triggered by electrical³ or optical⁴ excitations and by interface strain in case of epitaxial films on coherent substrates.^{5,6} The combination of these functional properties opens opportunity for creation of ultrafast electronic switches and memory elements.² The optical switching property of vanadium dioxide in the IR and THz ranges can be the base for new type of ultrafast optical devices (modulators, mirrors, lenses, metamaterials).^{7,8}

For electrical and optical applications the VO₂ thin films are the most prospective. The synthesis of VO₂ thin films with perfect MIT characteristics is a challenge because of low stability of the VO₂ phase to redox processes.⁹ The ability of vanadium to be in V²⁺, V³⁺, V⁴⁺ and V⁵⁺ oxidation states causes

the formation of nonstoichiometric vanadium oxides with variable oxygen content. The possible presence of the Magneli phases, defined by the general formula V_nO_{2n-1} (3 ≤ n ≤ 9) reduces the MIT characteristics of the films and complicates the interpretation of physical measurements.¹⁰ A number of physical vapor deposition methods have been employed for growth of vanadium dioxide thin films in both epitaxial and polycrystalline forms including PLD,^{6,11,12} sputtering,¹³ molecular beam epitaxy^{14,15} and ion beam deposition.¹⁶ Nevertheless the synthesis of vanadium dioxide films is complicated and requires careful control and maintenance of very low oxygen partial pressure in deposition chambers (the equilibrium p(O₂) of VO₂ is about 10⁻²⁴ atm at 600°C).¹⁷ This results in poor reproducibility of films composition and properties. The structural and physical properties of VO₂ films have been extensively studied, however the materials obtained by different research groups demonstrate a wide variety of the morphologies, phase compositions and physical properties due to the strong sensitivity of vanadium oxide to the growth process parameters.

Among chemical approaches to vanadium dioxide film synthesis a variety of CVD and metal-organic CVD (MOCVD) techniques has been reported. The CVD technique does not need a bulk target to prepare thin film material and ultrahigh vacuum system. It is a highly scalable industrial technology, which is able to produce high quality films of functional materials. The atmospheric pressure APCVD,¹⁸ low pressure LPCVD¹⁹ techniques and use of various precursors such as vanadyltrichloride,²⁰ vanadium(III) acetylacetonate,²¹ vanadyltriisopropoxide,²² triethoxide^{23,24} and diketonates of formula VOL₂ where L⁻ is acetylacetonate^{25,26} and hexafluoroacetylacetonate anion²⁷ have been tested. Nevertheless to this moment the chemical methods normally yield the VO₂ films with worse electrical and optical characteristics as compared to those of VO₂ films derived using PVD techniques.

^a Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia 119991.

^b SuperOx, 20/2 Nauchnyi proezd, Moscow, Russia 117246

^c Lomonosov Moscow State University, Department of Materials Science, Moscow, Russia 119991

^d Institute of Laser and Information Technologies RAS, Shatura, Russia 140700

^e Lomonosov Moscow State University, Department of Physics, Moscow, Russia 119991

[†] E-mail: makarevich@inorg.chem.msu.ru, Tel: +7 495 939 38 36.

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ARTICLE

In this paper we describe the original chemical preparation method based on LPMOCVD technique and postdeposition annealing, which allows to obtain high quality epitaxial VO₂ films demonstrating excellent electrical and optical properties comparable with the best ones reached by physical deposition techniques.

Experimental Section

Film deposition

The vanadium oxide films were obtained by LPMOCVD method in the hot-wall tubular vertical reactor (Fig. 1a) using the reaction between VO(hfa)₂ (98%, SuperOx) and water vapors in Ar atmosphere. Argon flow rate regulated by mass flow controller was 3.6 l/h. Water vapor was added into the system by microinjections of liquid water to the hot zone (100°C) with the rate 30 μl/min. The resulting pressure in the system was 3.5 mbar, 40% of which was the water vapor pressure. The temperature of precursor sublimation was 120°C. The temperature in the deposition zone was varied in the range 400–600°C. Films deposition was carried on the one side polished substrates of single crystal r-cut sapphire (r-Al₂O₃) cleaned by acetone and dried in air. This substrate was chosen since it is adopted in electronics, cheap and available of large size, possess of high thermoconductivity and the structure of r-plane is suitable for epitaxy of VO₂ films. The film growth process was *in situ* monitored by measuring of reflected laser beam (405 nm) intensity from the sample (Fig. 1b). Some of the samples after deposition at 400°C were annealed in the reactor at 600°C during 1 hour under low pressure (3 mbar, Ar flow 3.6 l/h). The growth rate (25–30 nm/min) was estimated as ratio of film thickness from TEM data (will be published elsewhere) to the deposition time determined from laser reflectometry (Fig. 1b).

Instrumentation

X-ray diffraction (XRD) studies of the samples were performed using Rigaku Smart Lab diffractometer equipped by X-ray generator with rotating copper anode. 2θ/ω- and φ-scans measurements were done in parallel beam geometry with Ge(220x2) monochromator (CuK_{α1} radiation). In order to investigate films texture in-plane pole figures for VO₂(200)/(-211) planes were measured with 1° steps for both φ- and χ-axes of scanning.

The surface textures of the films were analyzed by Electron Back Scatter Diffraction (EBSD) method using Jeol JSM-840A SEM and Oxford Instruments HKL Channel 5.

Raman spectra were recorded using a Renishaw InVia spectrometer under 785 nm laser at room temperature.

Film surface morphology was examined by scanning electron microscopy (SEM) using FEI Helios Nano Lab 600 DualBeam FESEM at 5 keV acceleration voltage and current 86 Pa in through-the-lens (TLD) regime.

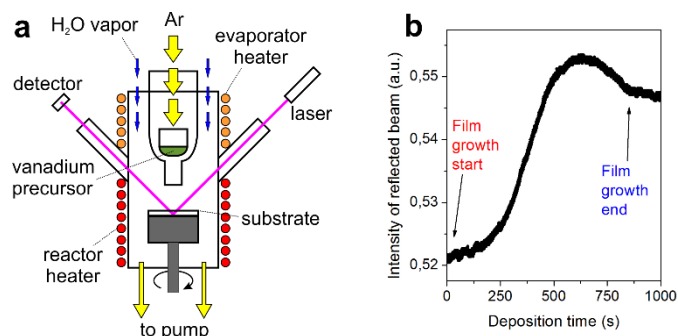


Fig. 1. Scheme of CVD device for deposition of VO₂ films (a). The example of deposition process *in situ* monitoring by measuring the intensity of reflected laser beam from substrate during the deposition process (b).

The atomic force microscopy (AFM) was performed on NTEGRA Aura (NT-MDT). The AFM instrument was operated in tapping mode using silicon probes Micro-Science N15 (tip radius < 10 nm). All AFM images were taken in air at room temperature.

X-ray photoelectron spectroscopy (XPS) measurement was performed on PHI 5000 Versa Probe with aluminium cathode and electron neutraliser. Spectrums was collect with pass energy of 23 eV. Linear energy correction was made in an accordance with carbone spectra. Energy of C_{1s} peak of non oxidized carbon was set as 284.8 eV. Ar⁺ sputtering was not applied to the films to prevent destruction of pristine surface.

The films resistance was measured with a standard four probe method in the temperature range 25–90°C (heating and cooling rate 1°C/min) using the Keithley 2700 multimeter.

Optical reflectance of films in IR range 400–4000 cm⁻¹ were investigated using FTIR spectrometer Perkin Elmer Frontier in temperature range 20–80°C (heating and cooling rate 1°C/min).

THz measurements were performed on the customized THz-TDS spectrometer. The source of THz radiation was the surface of LT-GaAs irradiated with 120 fs laser pulses at 800 nm wavelength. Electrooptical sampling with a 1 mm thick ZnTe crystal was used for detection allowing to study THz transmission in 0.1–2.5 THz range.

Results and Discussion

Film deposition

Among various vapor deposition techniques the chemical ones have some advantages for synthesis of materials due to the high flexibility of deposition process parameters by variability of precursor compositions and chemical reaction routes. In case of materials sensitive to oxygen partial pressure the chemical deposition technique using water vapor as an agent for metal-organic precursors destruction can be applied. This deposition method features preservation of oxidation state of metal ion on its way from metal-organic molecule to crystal structure of film material, that opens opportunity to *in situ* formation of stoichiometric vanadium dioxide films, that can be reached by vapor phase hydrolysis of volatile vanadium(IV) compounds:

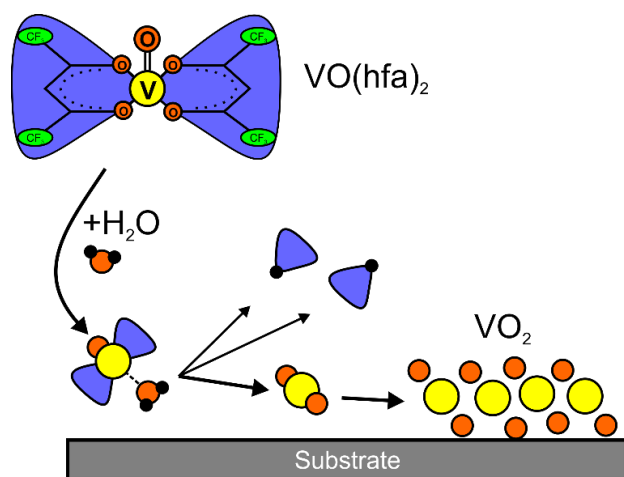
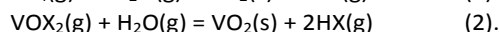
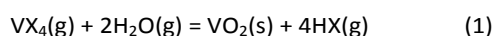


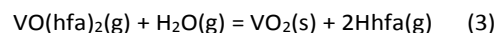
Fig. 2. The scheme of VO(hfa)₂ molecules pyrohydrolysis resulting in the VO₂ film growth.



The switch from oxidation reactions most used in MOCVD to the hydrolysis (or pyrohydrolysis at high temperature) processes (1) and (2) allows hypothetically to obtain the stoichiometric oxide phase VO₂ without admixtures of other vanadium oxides. Such reactions have low energetic activation barriers due to the exchange mechanism of the process: the protons from water molecule migrate to ligand anions that leads to elimination of ligands in protonated forms. As a result the film deposition using pyrohydrolytic reaction may be carried out in the mild conditions (<400°C).²⁸ The attempts of VO₂ film synthesis based on pyrohydrolysis reaction (1) were already realized using different deposition techniques and precursors: VCl₄ (atmospheric pressure MOCVD),²⁹ V(NEtMe)₄ (ALD).³⁰ These precursors are not comfortable for practical usage and the films obtained did not show sharp MIT. The pyrohydrolysis reaction (2) is more prospective because it allows to use vanadyl b-diketonates which are stable to storage, possess of high volatility and are commercially available. In 1999 in Barreca group the interaction between VO(dik)₂, where dik⁻ = 2,4-pentanedione (acac⁻), 2,2,6,6-tetramethyl-3,5-heptanedione (thd⁻), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (fod⁻) and water vapor in atmosphere of N₂ was investigated at temperature 380°C.²⁷ But only using of VO(hfa)₂ allowed to obtain the pure polycrystalline VO₂(M) films on Al₂O₃ substrates. The elimination of a protonated ligands Hhfa was confirmed by FTIR investigations and the low destruction of diketonates -C-C- chain during the reaction process was shown.²⁷ Unfortunately the physical properties of VO₂ films obtained by this method have not been presented by Barreca group.

In our laboratory we tested the precursors VO(acac)₂, VO(thd)₂ and VO(hfa)₂ (the result will be published elsewhere) for deposition of epitaxial VO₂ films and chose the vanadyl hexafluoroacetylacetonate as the most effective precursor (due to its lowest hydrolytic stability among these three) giving the best MIT characteristics of the films.

Our deposition experiments undertaken in the range 400-600°C showed that the reaction (Fig. 2)



is highly reproducible giving always VO₂ phase that was confirmed by XRD and Raman spectroscopy. The precursors flow rates influenced remarkably the film quality. The formation of the uniform films took place in case of the VO(hfa)₂ and H₂O flow rates 7.5·10⁻⁶ mol/min and 2.2·10⁻³ mol/min, respectively. From these data it can be seen that in the reaction zone there is large excess of water vapor (molar ratio of VO(hfa)₂ to H₂O was equal 1:300) for promotion of hydrolysis reaction. At 400°C such flow rates resulted in film growth rate 30 nm/min. The higher film growth rate (>100 nm/min) leads to rough films surface morphology because of powder precipitation from gas phase that, evidently, resulted from homogeneous nucleation at high supersaturation.

Our deposition experiments were carried out in argon flow with the residual oxygen partial pressure 10⁻⁵ atm according to the measurements with the electrochemical sensor attached to the deposition reactor. This is of course high enough for VO₂ oxidation (compare with equilibrium p(O₂) = 10⁻²⁴ atm at 600°C).¹⁷ We believe that at the deposition temperature the kinetics of oxidation is low enough and the vanadium oxide does not reach equilibrium composition in the depth of the deposited film. At the same time partial surface oxidation of VO₂ grains takes place as it was confirmed by XPS analysis (see paragraph below). We suppose that the oxidation occurs in a very thin skin layer of the grains building the film structure.

Post-deposition annealing

Among the factors influencing on the MIT characteristics the VO₂ film granularity is of big importance. The films consisting of the grains with poor connectivity and partly oxidized intergrain boundary layers showed wide hysteresis loops with diminished MIT values. For example, V₆O₁₃ at temperature above 150 K shows metallic behavior and its presence at the grain boundaries leads to decreasing of VO₂ films resistance in the insulator phase. In contrast the presence of semiconducting V₂O₅ between VO₂ grains can increase remarkably the resistance values of films in metal state. As a result the films containing oxidized phases VO_{2+x} between VO₂ grains show poor resistance change amplitude at MIT.

For optimization of VO₂ film switching properties it is necessary to improve grain connectivity and to activate the process of crystallites growth. In our work we tried to improve the MIT characteristics by i) increasing the deposition temperature from 400 to 600°C and by ii) the post-deposition annealing.

The best result was reached in case of additional heat treatment at 600°C of VO₂ films deposited at 400°C. In our experiments we showed, that the annealing at 600°C lead to intensive VO₂ grains association process. This fact seems to be unusual because the annealing temperature 600°C is remarkably lower than Tamman's temperature determined as 0.6 of VO₂ melting temperature (~1813 K).³¹ To our opinion, the features of the V-O phase diagram (Fig. 3) can explain this phenomenon. According to it, the presence of phases containing V⁺⁵ as admixture to VO₂ drastically decreases the

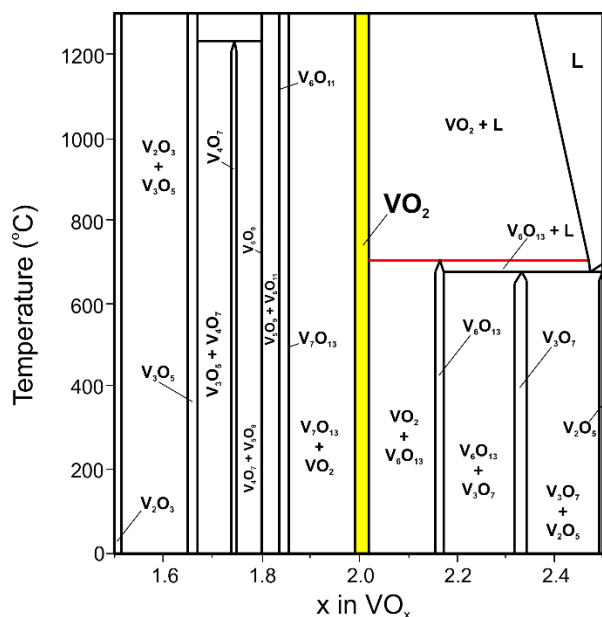
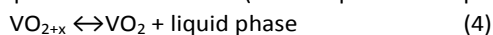


Fig. 3. The $V_2O_3 - V_2O_5$ phase diagram.³¹

temperature of partial melting due to peritectic decomposition of V_6O_{13} and V_3O_7 phases. So, even minor amounts of oxidized phases (marked as VO_{2+x}) on the VO_2 crystallites boundaries play the role of flux and activate fast grain recrystallization process. Peritectic reaction results in formation of additional quantities of VO_2 phase from oxidized phases VO_{2+x} at temperatures near 700°C (for bulk phases in equilibrium state):



and this "cleans" intergranular contacts.

It is worthy to note that the intensive recrystallization already occurs at 600°C , while the peritectic reaction (4) in equilibrium bulks occurs at 708°C . Indeed, the temperatures of solid state equilibria are normally remarkably lower for nanoparticles, nanoparticulate solids and thin films.

For efficient recrystallization the peritectic melt at the grain boundaries should be distributed between small VO_2 grains and this is realized in the annealing of the films.

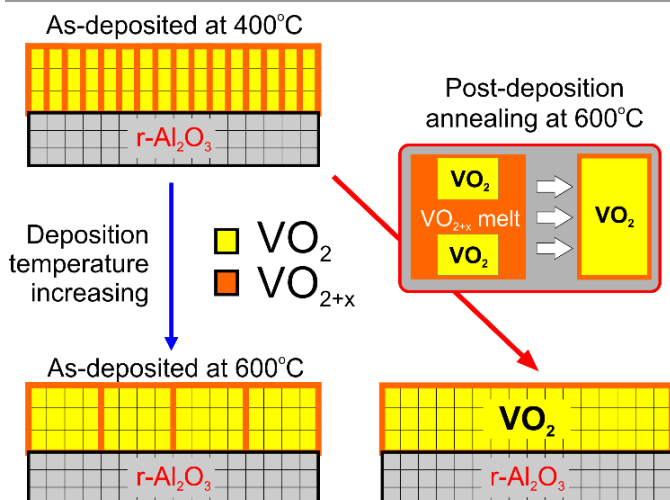


Fig. 4. The scheme of VO_2 films growth in dependence of the synthesis conditions.

deposited at 400°C . The films deposited at 600°C according to our SEM data consist of much larger VO_2 crystallites. We believe, that these crystallites are also divided by partly oxidized skin layers, but due to the size effect the quantity of peritectic melt is not enough for efficient recrystallization (see Fig. 4).

Films characterization

The results of θ - 2θ X-ray analysis of the films as-deposited and after annealing are presented in Fig. 5a.

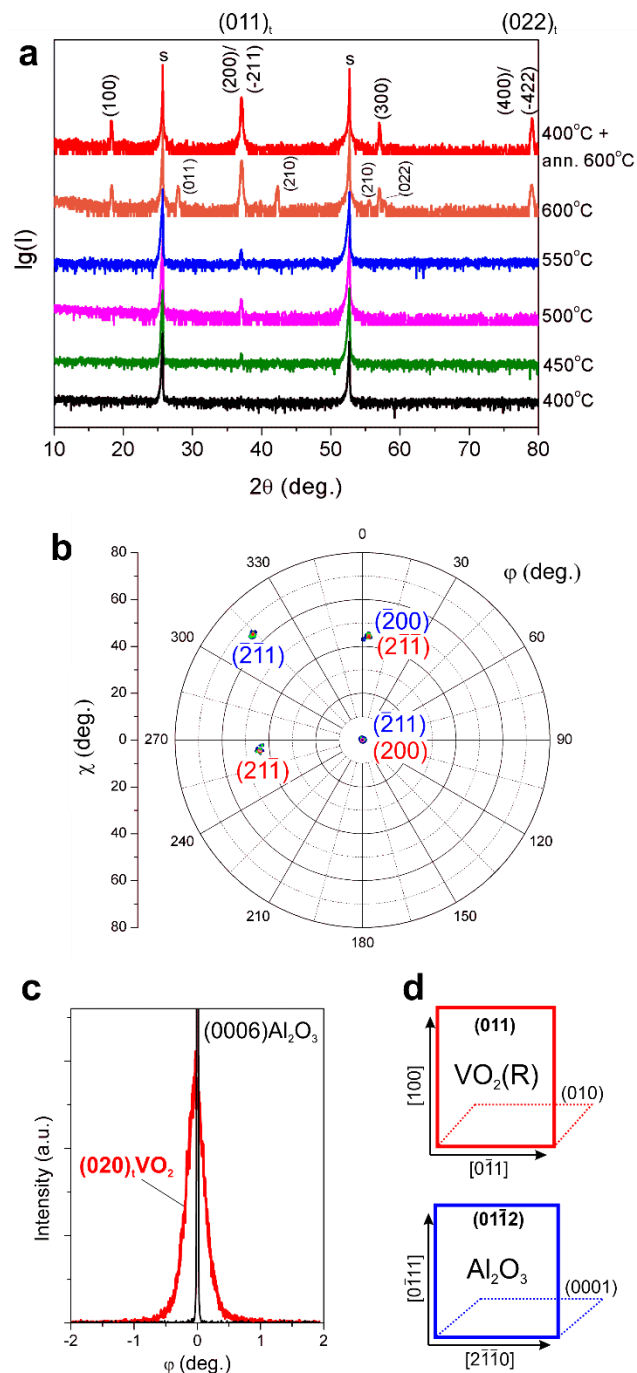


Fig. 5. The results of XRD analysis of $VO_2/r\text{-Al}_2O_3$ films. The 2θ -scan for samples obtained in the temperature range $400\text{-}600^\circ\text{C}$ (a). The pole figure at $2\theta = 37.14^\circ$ of VO_2 film after annealing (b). The ϕ -scan of $VO_2(R)/r\text{-Al}_2O_3$ film after annealing (c). The epitaxial relationships between $VO_2(R)$ film and $r\text{-Al}_2O_3$ substrate (d).

The film deposited at 400°C gave poor diffraction picture that did not give an opportunity to define the phase composition. At temperature range 450-550°C the X-ray patterns were presented only by single reflection at 37.14° corresponding to the (200) and (-211) planes of VO₂(M) (in the following text it is marked as (200)/(-211) (ICDD card [43-1051]).

The sample obtained at 600°C showed the X-ray pattern containing several intensive reflections, which indicated the formation of VO₂(M) phase with good crystalline structure. The high intensities of peaks at 18.30, 37.14, 56.97 and 79.06° corresponding to crystallographic plane series (100), (200)/(-211), (300) and (400)/(-422), respectively, can be explained by active epitaxial growth at this temperature. However, the presence of addition reflections at 27.9, 42.3, 55.6 and 57.7° corresponding to (011), (210), (211) and (022) of VO₂(M), respectively, showed also the formation of polycrystalline part of the film. In case of post-annealed film the X-ray pattern for pure (100)/(-211) orientation of VO₂(M) without impurities of other phases or orientations was obtained.

The epitaxial growth of VO₂ films on r-Al₂O₃ substrates was confirmed by pole figure obtained at 2θ = 37.14° showing the presence of four reflections related to the superpositions of two orientations of VO₂(M) (Fig. 5b).⁶ Simplified epitaxial relationships between film and substrate can be described for VO₂(R) phase (ICDD card [42-0253]) which has the tetragonal structure closed to the monoclinic structure of VO₂(M) phase with light distortion. The (200)/(-211) reflection on 2θ-scan of monoclinic phase is related to the (011) reflection of tetragonal phase. So the out-of-plane film orientation is (011)VO₂(R) || (01-12)Al₂O₃. The film orientation in surface plane was analyzed by φ-scanning of (020)VO₂(R) and (0006)Al₂O₃ reflections (Fig. 5c). These peaks had the same positions on the φ-scan that showed the formation of following orientations: VO₂[0-11] || Al₂O₃[2-1-10] and VO₂[001] || Al₂O₃[0-1110] (Fig. 5d). The transformation matrixes for transition from tetragonal VO₂(R) to monoclinic VO₂(M) crystal cells and epitaxial relationships between VO₂(M) and r-Al₂O₃ substrate are presented in the Electronic Supplementary Information. The similar orientations were demonstrated by Narayan group for VO₂/r-Al₂O₃ films obtained by PLD method.⁶

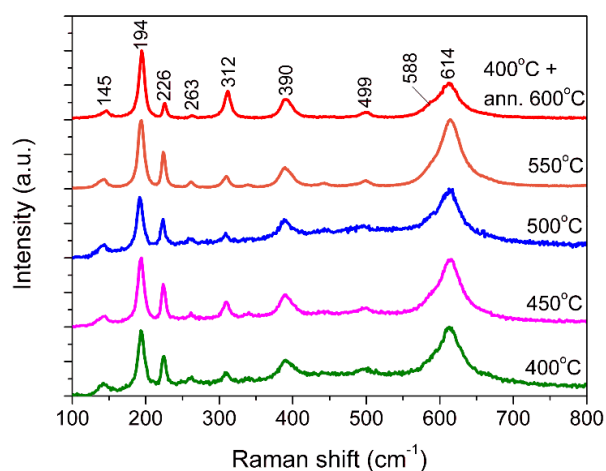


Fig. 6. The Raman spectra for VO₂/r-Al₂O₃ films obtained at different temperatures.

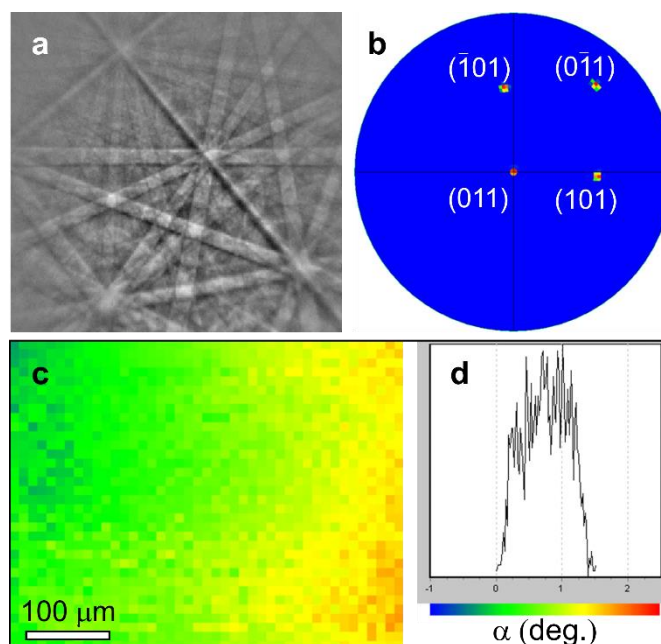


Fig. 7. The result of EBSD analysis of VO₂/r-Al₂O₃ film: example of Kikuchi lines (a), pole figure for (011)VO₂(R) (b) and texture map (c) with histogram of surface crystallites disorientation (d).

The phase composition of the films obtained at temperature range 400-550°C was also studied using the Raman spectroscopy (Fig. 6). The spectra characters were similar for all samples and contained the typical peaks 145(A_g), 194(A_g), 226(A_g), 263(B_g), 312(A_g, B_g), 390(A_g), 499(A_g), 588(B_g), 614(A_g) cm⁻¹ corresponding to the monoclinic VO₂ M₁ phase.³² Even the spectrum of the film deposited at 400°C shows the presence of M₁ phase, while in XRD the film gave no detectable diffraction could result from the poor texturing of the sample at low deposition temperature.

For comparison the post-annealed sample also was analyzed and it is necessary to note that additional treatment resulted in some changes in the peaks intensity that can be explained by high texture formation. The most significant intensity changes were found for Raman shifts at 194 and 312 cm⁻¹. The similar behavior of peaks intensity distribution has been reported previously for epitaxial VO₂ films deposited on the sapphire substrates.³³

The film deposited at 400°C and post-annealed at 600°C was analyzed also by EBSD method since the technique is useful for surface phase crystal structure description. The result Kikuchi lines (Fig. 7a) were clear and intensive that showed the high crystallinity and surface orientation of the film. The attempt to describe the structure as monoclinic one was not fruitful because the treatment of Kikuchi lines gave no difference in two possible alternative M₁ VO₂ phase orientations, thus the film structure was described as tetragonal VO₂ of rutile type. This analysis confirmed the formation of VO₂ crystallites with sharp biaxial texture (FWHM ~0.7°), the related pole figure was similar to one obtained from XRD (Fig. 7b,c).

Table 1. The XPS data for VO₂ films deposited at 400°C: as-deposited (1) and post-annealed at 600°C (2).

Sample	V ⁿ⁺	V2p _{3/2}	FWHM	Percentage
1	V ⁵⁺	517.3	1.70	32(1)
	V ⁴⁺	516.0	1.37	68(2)
2	V ⁵⁺	517.1	1.67	31(1)
	V ⁴⁺	515.8	1.30	69(2)

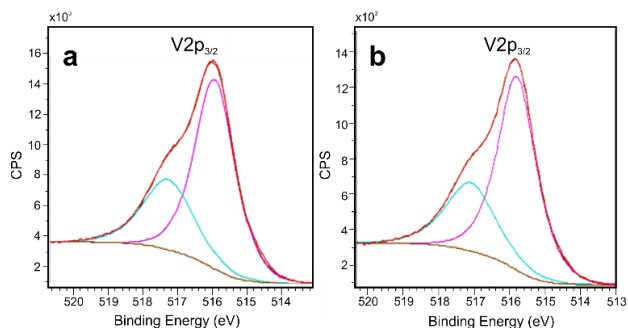


Fig. 8. The XPS analysis of VO₂/r-Al₂O₃ films: (a) as-deposited at 400°C, (b) post-annealed at 600°C.

The elemental surface composition of the films as-deposited at 400°C and after annealing was analyzed by XPS method. The F1s spectrum (670–680 eV) did not demonstrated any signals of fluorine atoms that allowed us to establish that the pyrohydrolysis reaction (3) proceeds without parasitic fluorine contamination. Analysis of the region of V2p_{3/2} at 513–521 eV (Fig. 8b) according to the literature data showed that the film contain vanadium in oxidation states V⁴⁺ and V⁵⁺.^{34,35}

Unfortunately the XPS does not allow us to estimate the composition and oxidation state of ions in the volume of the film due to short free path of analytical electron in solid state and destructive influence of Ar⁺ sputtering to the pristine surface.³⁴ Both samples demonstrated the same analytical results - ratio of V⁵⁺ to V⁴⁺ was 8:17 (Table 1). The rough estimation of x value in VO_{2+x} layer from XPS data gave value of 0.16 that is very close to V₆O₁₃ (0.167) – the phase in equilibrium with VO₂ on the phase diagram. Thus, the XPS is the only method showing the presence of oxide containing more oxygen than VO₂.

The results of scanning electron microscopy of the films VO₂/r-Al₂O₃ are presented in Fig. 9. The sample obtained at 400°C consisted of anisotropic particles with size of 50–70 nm. Increasing of deposition temperature lead to growth of crystallites size (Fig. 9b–e). The VO₂ film as-deposited at 600°C consisted of well-shaped column type crystallites having the lateral size 400–500 nm.

The annealing at 600°C of the sample deposited at 400°C leads to microstructure with no clear grain boundaries indicating the effective crystallites association but with visible subgrains alignment. The difference in morphology of as-deposited and post-annealed VO₂ films confirms the above discussed scenario of peritectic reaction (see the Section “Post-deposition annealing”). Regarding the effect of deposition temperature we can conclude, that under conditions of deposition process we obtained the films consisted of the particles shelled with the VO_{2+x} skin layer but in case of the film

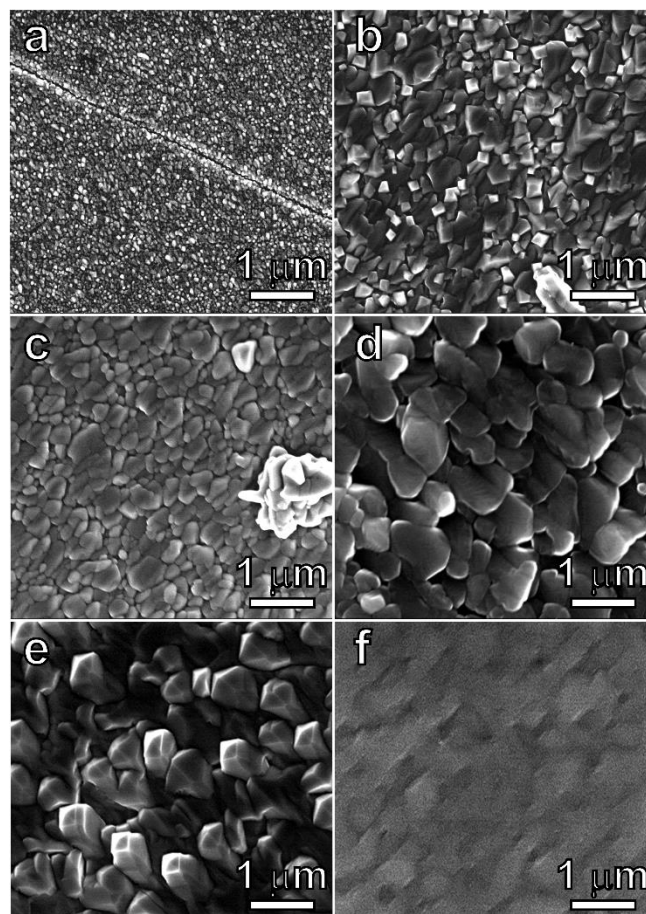


Fig. 9. The SEM analysis of VO₂/r-Al₂O₃ films obtained at different temperatures: 400°C (a), 450°C (b), 500°C (c), 550°C (d), 600°C (e) and after annealing at 600°C of film deposited at 400°C (f).

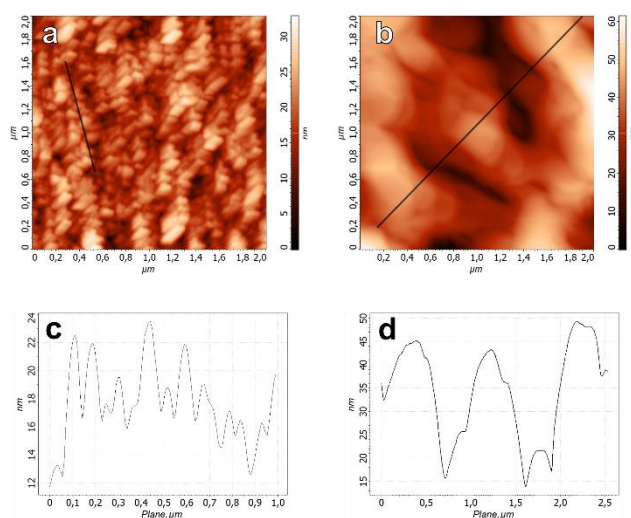


Fig. 10. The AFM analysis of VO₂/r-Al₂O₃ films: the scanning maps (a,b) and profiles (c,d) across the black lines of the film as-deposited at 400°C (a,c) and one post-annealed at 600°C (b,d).

obtained at 400°C the intergrain surface area was much higher than in case of the sample deposited at 600°C that led to higher concentration of oxidized phases, decomposing peritectically at 600°C and thus promoting more efficient coalescence of VO₂ grains.

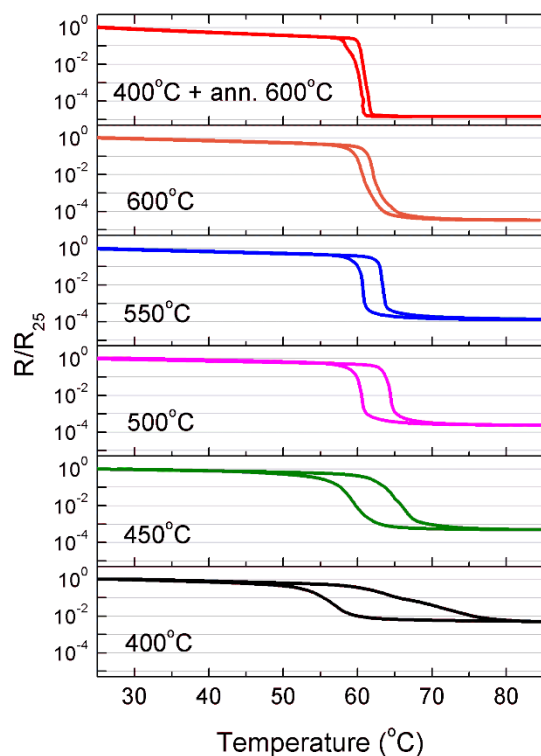


Fig. 11. The MIT characteristics of $\text{VO}_2/\text{r-Al}_2\text{O}_3$ films obtained at different temperatures: the definition of the main MIT parameters (a) and their changes in dependence the deposition temperature (b, c). The characteristics of sample obtained by post-annealing at 600°C are marked by star symbols.

The morphology of the films as-deposited at 400°C and post-annealed at 600°C was also investigated by AFM method. The results shown in Fig. 10 confirm the results of SEM analysis and allow us to see the film surface in detail. It was found that the deposition at 400°C lead to the formation of the film of low roughness ($S_a = 3.7 \text{ nm}$, $S_q = 4.6 \text{ nm}$), which consisted of the biaxial textured crystallites with maximum lateral size of 100 nm (Fig. 10a,c). The thermal treatment at 600°C results in strong increase of both grain size (Fig. 10b,d) and surface roughness ($S_a = 11.2 \text{ nm}$, $S_q = 14.8 \text{ nm}$). The similar morphological effects were reported for the VO_2 films obtained by PLD technique at temperatures $600\text{--}650^\circ\text{C}$.^{6,36}

Electrical and optical properties

A standard four probe method was used for the characterization of the transport properties of vanadium dioxide films on $\text{r-Al}_2\text{O}_3$ in the range $20\text{--}85^\circ\text{C}$. The temperature dependences of the electrical resistance and the main MIT parameters (T_{MIT} , ΔT , ΔR) of the films are presented in the Fig. 11 and 12. The T_{MIT} for all of the samples are near 60°C that is remarkably lower in comparison with T_{MIT} of bulk material (68°C), the difference is usually attributed to the effect of the strain caused by mismatch at the interface of VO_2 film and r-sapphire substrate.^{6,33} Increasing of deposition temperature leads to decreasing of T_{MIT} from 62.9 to 61.3°C and it correlates with the improvement of biaxial texture quality. The films deposited at higher temperatures possess better crystallinity and of sharper texture which originates at the interface, thus

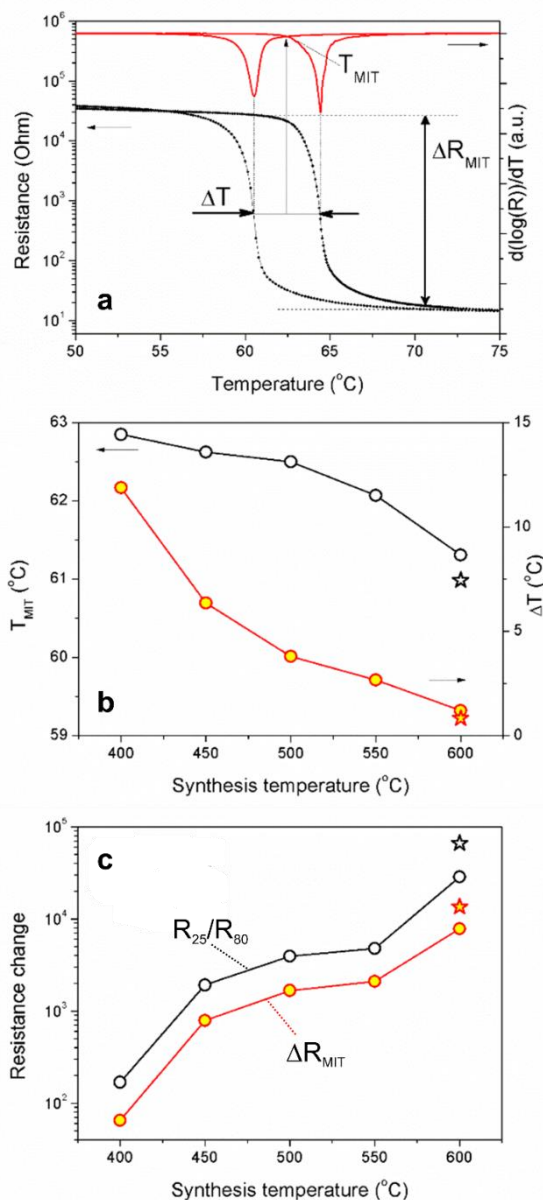


Fig. 12. The MIT characteristics of $\text{VO}_2/\text{r-Al}_2\text{O}_3$ films obtained at different temperatures: the definition of the main MIT parameters (a) and their changes in dependence the deposition temperature (b, c). The characteristics of sample obtained by post-annealing at 600°C are marked by star symbols.

the stronger is the film-substrate interaction at the interface, the more strained is the film and this results in T_{MIT} decrease.

The increase of deposition temperature also influenced on the hysteresis loop width (ΔT): it decreased from 11.9 to 1.2° for $T_{\text{dep}} = 400^\circ\text{C}$ and 600°C , respectively. It can be seen that as-deposited film is characterized by low MIT amplitude ($R_{25}/R_{80} = 170$; $\Delta R_{\text{MIT}} = 65$), but increasing of synthesis temperature to 600°C highly improved the value of resistivity change to $2.8 \cdot 10^4$ ($\Delta R_{\text{MIT}} = 7.8 \cdot 10^3$). The sample after annealing demonstrates the highest resistance change ($R_{25}/R_{80} = 6.6 \cdot 10^4$) with $\Delta R_{\text{MIT}} = 1.4 \cdot 10^4$. The comparison with the published data on VO_2 films confirms that the transport characteristics of annealed sample belong to the best ones among known for epitaxial thin films obtained on $\text{r-Al}_2\text{O}_3$ by different chemical and physical methods.

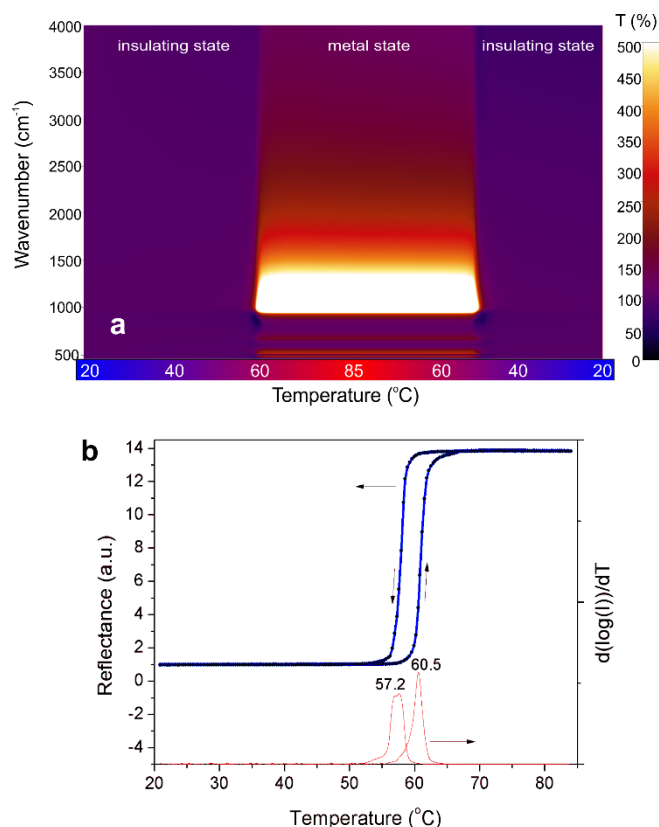


Fig. 13. The reflectivity properties of $\text{VO}_2/\text{r-Al}_2\text{O}_3$ films deposited at 400°C and post-annealed at 600°C : the 2D map in the range $400\text{--}4000\text{ cm}^{-1}$ (a), the temperature hysteresis loop for wavenumber 1000 cm^{-1} (b).

IR reflectivity of annealed sample were measured in the range of $400\text{--}4000\text{ cm}^{-1}$ in dependence on the temperature from 25 to 90°C (Fig. 13a). It was found that approaching 60°C the sample began to show reflectivity properties typical for metal state, but the difference in reflectivity of insulating and metal phases demonstrates nonlinear dependence on IR wave number with the maximum at 1000 cm^{-1} and the reflectance change more than 14 times (Fig. 13b).

Worthy to note is that for the film deposited at 400°C and post-annealed at 600°C the ΔT_{MIT} observed in optical measurements is distinctly larger than that from electrical measurements (3.3°C and 1.5°C , respectively). The reason is the film obtains the metallic conductivity only when the conductive domains or grains form the percolation chains along the substrate. In contrast, the reflectance of the film does not need percolation and even isolated domains with high concentration of electronic carriers are not transparent in the IR range. No doubt, these separated domains appear before the percolation chains arise during heating of VO_2 film and they disappear after the percolation chains are destroyed when the film is cooled down through the MIT temperature range.

Studies of transmission coefficient in $0.1\text{--}2.5\text{ THz}$ spectral range were performed in standard THz time-domain spectrometer in transmission scheme at normal laser beam incidence. The spectra of transmitted radiation in both insulating and metallic states of the VO_2 film post-annealed at

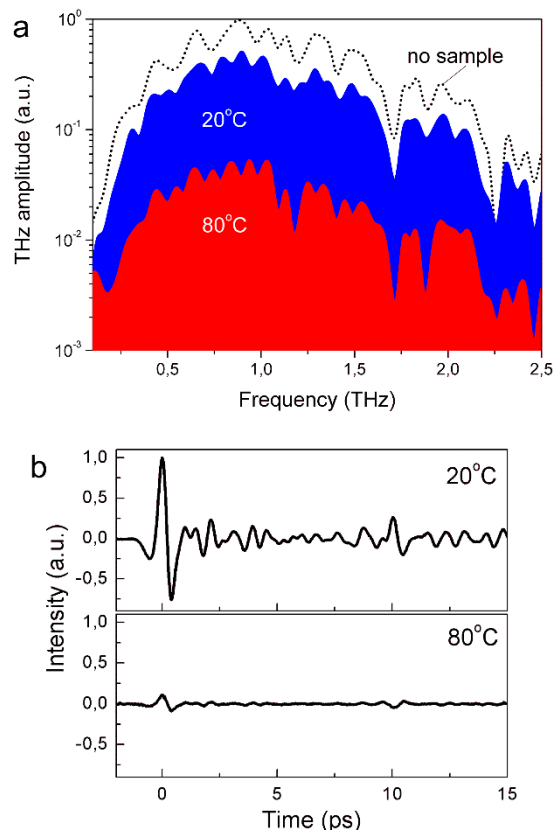


Fig. 14. The THz transmission properties before and after MIT of $\text{VO}_2/\text{r-Al}_2\text{O}_3$ films post-annealed at 600°C : the transmission coefficient (a), the transmission spectrum in $0.1\text{--}2.5\text{ THz}$ range (b).

600°C are shown in the Fig. 14a. A substantial transmittance decrease in the range $0.1\text{--}2.5\text{ THz}$ was observed for metallic state above T_{MIT} with the maximum effect reaching about 90% at 1 THz (Fig. 14a,b). This result shows that the high quality VO_2 films obtained are the materials very interesting for practical applications in THz range.

Conclusions

In this work we introduced new effective chemical approach to obtaining of the high quality epitaxial vanadium dioxide films on r-sapphire substrates. The synthesis method is based on the two steps: 1) LPMOCVD of VO_2 films by the reaction between vanadyl hexafluoroacetylacetonate and water vapors in inert atmosphere and 2) the post-annealing of the films at 600°C leading to active recrystallization and resulting in formation of film structure with tight grains connection. The theory of VO_2 films recrystallization process based on the peritectic decomposition of the oxidized thin shell of VO_{2+x} surrounding VO_2 grains was proposed. The films obtained by this technique demonstrate excellent electrical and optical MIT characteristics: the resistance change more than 4 orders of magnitude, IR reflectance change in 14 times (at 1000 cm^{-1}) and THz transmittance change by 90% (at 1 THz).

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References

- L.A. Ladd and W. Paul, *Solid State Commun.*, 1969, **7**, 425.
- Z. Yang, C. Ko and S. Ramanathan, *Annu. Rev. Mater. Res.*, 2011, **41**, 337.
- B.G. Chae, H.T. Kim, D.H. Youn and K.Y. Kang, *Physica B*, 2005, **369**, 76.
- M. Liu, H.Y. Hwang, H. Tao, A.C. Strikwerda, K. Fan, G.R. Keiser, A.J. Sternbach, K.G. West, S. Kittiwatanakul, J. Lu, S.A. Wolf, F.G. Omenetto, X. Zhang, K.A. Nelson and R.D. Averitt, *Nature*, 2012, **487**, 345.
- J. Li and J. Dho, *J. Crystal Growth*, 2010, **312**, 3287.
- T.H. Yang, R. Aggarwal, A. Gupta, H.Zhou, R. J. Narayan and J. Narayan, *Appl. Phys.*, 2010, **107**, 053514.
- M. Nakano, K. Shibuya, N. Ogawa, T. Hatano, M. Kawasaki, Y. Iwasa and Y. Tokura, *J. Appl. Phys. Lett.*, 2013, **103**, 153503; M.J. Dicken, K. Aydin, I.M. Pryce, L.A. Sweatlock, E.M. Boyd, S. Walavalkar, J. Ma and H.A. Atwater, *Optic Express*, 2009, **17**, 20, 18330; H.S. Choi, J.S. Ahn, J.H. Jung, T.W. Noh and D.H. Kim, *Phys. Rev. B*, 1996, **54**, 7, 4621.
- M.A. Kats, R. Blanchard, S. Zhang, P. Genevet, C. Ko, S. Ramanathan and F. Capasso, *Phys. Rev. X*, 2013, **3**, 041004; M. Seo, J. Kyoung, H. Park, S. Koo, H.S. Kim, H. Bernien, B.J. Kim, J.H. Choe, Y.H. Ahn, H.T. Kim, N. Park, Q.H. Park, K. Ahn and D.S. Kim, *Nano Lett.*, 2010, **10**, 2064; P.U. Jepsen, B.M. Fischer, A. Thoman, H. Helm, J.Y. Suh, R. Lopez and R.F. Haglund, *Phys. Rev. B*, 2006, **74**, 205103.
- C.H. Griffiths and H.K. Eastwood, *Appl. Phys.*, 45, **5**, 2201.
- D. Vernardou, M.E. Pemble and D.W. Sheel, *Chem. Vap. Dep.*, 2006, **12**, 263.
- D.H. Kim and H.S. Kwok, *Appl. Phys. Lett.*, 1994, **65**, 25, 3188.
- M. Borek, F. Qian, V. Nagabushnam and R.K. Singh, *Appl. Phys. Lett.*, 1993, **63**, 24, 3288.
- P. Mandal, A. Speck, C. Ko and S. Ramanathan, *Optic Lett.*, 2011, **36**, 10, 1927.
- N.F. Quackenbush, J.W. Tashman, J. A. Mundy, S. Sallis, H. Paik, R. Misra, J.A. Moyer, J.-H. Guo, D.A. Fischer, J.C. Woicik, D.A. Muller, D.G. Schlom and L.F.J. Piper, *Nano Lett.*, 2013, **13**, 4857.
- J.W. Tashman, J.H. Lee, H. Paik, J.A. Moyer, R. Misra, J.A. Mundy, T. Spila, T.A. Merz, J. Schubert, D.A. Muller, P. Schiffer and D.G. Schlom, *Appl. Phys. Lett.*, 2014, **104**, 063104.
- J. Li, N. Yuan and J. Xie, *Appl. Surf. Science*, 2005, **243**, 437.
- J.B. MacChesney and H.J. Guggenheim, *J. Phys. Chem. Solids*, 1969, **30**, 225.
- T.D. Manning, I.P. Parkin, M.E. Pemble, D. Sheel and D. Vernardou, *Chem. Mater.*, 2004, **16**, 744.
- M.B. Sahana, G.N. Subbanna and S.A. Shivashankar, *J. Appl. Phys.*, 2002, **92**, 11, 6495.
- T. Szorenyi, K. Bali and I. Hevesi, *J. Non-Cryst. Solids*, 1980, **35-36**, 1245.
- T. Maruyama and Y. Ikuta, *J. Mater. Sci.*, 1993, **28**, 5073.
- C.B. Greenberg, *Thin Solid Films*, 1983, **110**, 73.
- H.L.M. Chang, Y. Gao, T. J. Zhang and D. J. Lam, *Thin Solid Films*, 1992, **216**, 4.
- H. Zhang, H.L.M. Chang, J. Guo and T. J. Zhang, *J. Mater. Res.*, 1994, **9**, 2264.
- M.B. Sahana, M.S. Dharmaprakash and S.A. Shivashankar, *J. Mater. Chem.*, 2002, **12**, 333.
- X. Zhong, P. LeClair, S.K. Sarker and A. Gupta, *Phys. Rev. B*, 2012, **86**, 094114.
- D. Barreca, L.E. Depero, E. Franzato, E. Tondello, G.A. Rizzi, U. Vettori and L. Sangaletti, *J. Electrochem. Soc.*, 1999, **146**, 2, 551.
- A. Makarevich, A.Shchukin, A. Markelov, S. Samoilenkov, P. Semyannikov and N. Kuzmina, *Electrochem. Soc. Trans.*, 2009, **25**, 8, 525.
- D. Vernardou, M.E. Pemble and D.W. Sheel, *Chem. Vap. Depos.*, 2006, **12**, 263.
- K. Zhang, M. Tangirala, D. Nminibapiel, W. Cao, V. Pallem, C. Dussarrat and H. Baumgart, *Electrochem. Soc. Trans.*, 2012, **50**, 13, 175.
- K. Kosuge, *Phys. Chem. Solids*, 1967, **28**, 8, 1613; H.A. Wriedt, *Bull. Alloy Phase Diagrams*, 1989, **10**, 3, 271.
- X. Chen, *J. Korean Phys. Soc.*, 2011, **58**, 1, 100.
- Y. Zhao, J.H. Lee, Y. Zhu, M. Nazari, C. Chen, H. Wang, A. Bernussi, M. Holtz and Z. Fan, *J. Appl. Phys.*, 2012, **111**, 053533.
- E. Hryha, E. Rutqvistb and L. Nyborga, *Surf. Interface Anal.*, 2012, **44**, 1022.
- M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, *Appl. Surf. Sci.*, 2010, **257**, 887.
- B.J. Kim, Y.W. Lee, S. Choi, B.G. Chae and H.T. Kim, *J. Korean Phys. Soc.*, 2007, **50**, 3, 653.

The new effective chemical synthesis of the epitaxial VO_2 films with record electrical and optical switch properties is presented.

